

Photochemical Sinks of Organic Pollutants in Estuarine and Near-Shore Environments

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LONG-TERM GOALS

The principal objective of this work has been to assess the quantitative importance of homogenous and heterogeneous photochemistry as a sink of pollutants in the aquatic environment. Using a combination of chemical trapping techniques, steady-state and time-resolved spectroscopic methods and product analysis, we have examined the mechanisms and magnitude of the photochemical production of strong oxidants and reductants by chromophoric dissolved organic matter (CDOM), as well as how these species may contribute to the degradation of common pollutants such as polycyclic aromatic hydrocarbons and halogenated organic compounds. The relative contributions of both the direct and sensitized photochemical destruction of these pollutant classes is under investigation. Ultimately, we plan to employ the information acquired from these studies to develop simple models that can be utilized to predict the photochemical rates of pollutant loss.

OBJECTIVES

Over the last year, our principal near-term objectives were as follows:

1. Prepare and publish a manuscript on the magnitude of both the direct and sensitized photochemical destruction of polycyclic aromatic hydrocarbons (PAH's) in pure and natural waters. Acquire data for a second manuscript on the mechanisms of the primary reactions leading to their direct photodegradation in aqueous systems.
2. Prepare and publish a manuscript on the aqueous photochemistry of 2-methyl-1,4-benzoquinone, a representative example of environmentally-relevant compounds capable of generating an oxidizing intermediate. Acquire additional data on the nature of the oxidizing intermediate that is produced in a series of 1,4-benzoquinones.

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APPROACH

The first objective was achieved by following the rates of the direct or sensitized loss of PAHs using either reversed-phase HPLC with fluorometric detection or steady-state fluorescence. Product analysis is ongoing. A series of 12 PAHs are currently being examined. These PAHs exhibit a broad range of structures and molecular properties, allowing us to probe the factors controlling their direct photodegradation in aqueous solution.

The second objective was achieved through a combination of laser flash photolysis studies and chemical trapping studies.

WORK COMPLETED

1. Published our work on the aqueous photodegradation of a series of 12 PAHs (Fasnacht and Blough, 2002; see abstract below which summarizes our findings). An additional manuscript, which addresses the mechanisms of the primary photochemical reactions in this series of PAHs, is currently being prepared for publication (Fasnacht and Blough, in preparation).
2. Published our work on the aqueous photochemistry of 2-methyl-1,4-benzoquinone (Pochon et al., 2002; see abstract below that summarizes our findings). An additional manuscript, which examines the nature and yield of the oxidizing intermediate in a series of 1,4-benzoquinones, is currently being prepared for publication (Gan et al., in preparation).

RESULTS

Photodegradation of 12 PAHs was studied in aerated pure water, solutions of Suwannee River fulvic acid, and natural waters using polychromatic light (>290 nm). Quantum yields in pure water varied widely, from 3.2×10^{-5} for fluoranthene to 9×10^{-3} for acenaphthene. No obvious relationships were evident among the quantum yields and molecular properties. Photodegradation rate constants in solutions of Suwannee River fulvic acid or natural waters were largely unchanged compared to rate constants in pure water, indicating that this material neither sensitizes nor protects the PAHs. Estimates of PAH photodegradation rates in natural waters can thus be obtained employing the quantum yields in pure water, PAH absorption and solar irradiance. Calculated rate constants for photodegradation in an optically-thin section of surface waters during the summertime at mid-latitude varied from a low of $3.2 \times 10^{-7} \text{ hr}^{-1}$ for fluorene to a high of 7.6 hr^{-1} for benzo[a]pyrene.

The quantum yields for most of these PAHs exhibit a strong, but not identical, dependence on dioxygen concentration. This dependence can be attributed to reactions occurring through both the excited triplet and singlet states (Fasnacht and Blough, 2002). Modeling results indicate that some PAHs such as pyrene and benzo[a] pyrene react almost exclusively through the singlet, whereas others, such as anthracene, appear to react predominantly through the triplet (Fasnacht and Blough, in preparation). Present work is focusing on identify the intermediates produced in these reactions.

Photolysis of 2-methyl-1,4-benzoquinone (toluquinone) in aqueous solution results in the oxidation of water to create either hydroxyl radical or some species capable of transferring a hydroxyl radical. Trapping of the latter with dimethyl sulfoxide (DMSO) creates a methyl radical which in turn can be trapped by the stable radical 3-amino-2,2,5,5-tetramethyl-1-pyrrolidinyloxy. Competitive trapping

studies using DMSO and either nitrite anion or salicylate anion show that the hydroxylating species is much more selective in its reactions than free hydroxyl radical. Laser flash photolysis experiments on toluquinone in aqueous solution show formation of a transient species immediately (<150 ns) following the excitation pulse that had previously assigned to the excited triplet state of the quinone. This spectrum differs from the authentic triplet state spectrum generated in less reactive organic solvents (carbon tetrachloride and acetonitrile). The same intermediate is shown to react with the hydroxyl radical traps, cupric ions and benzoate anion to yield the semiquinone radical. On this basis of these experiments it is argued that this transient species is a hydroxylating intermediate, probably best described as a complex between the semiquinone radical and the hydroxyl radical. It is further argued that this species is responsible for the hydroxyl radical trapping reactions.

Further work has shown that dimethyl-quinones and dichloroquinones also produce a strong oxidant that cannot be attributed to the hydroxyl radical alone. In contrast, tetrachloroquinone (chloranil), which has a much more favorable thermodynamic driving force for electron transfer from water, does appear to release free hydroxyl radical, consistent with our idea that OH release will occur as the thermodynamic driving force for electron transfer from water becomes more favorable (Gan et al., in preparation).

IMPACT/APPLICATIONS

This work has allowed us to gain a better understanding of the rates and mechanisms of the photochemical degradation of both natural and anthropogenic compounds in natural waters. This knowledge should, in turn, help us to develop predictive models for the photochemical destruction of new compounds released to the environment.

TRANSITIONS

The radical trapping approach that we have continued to develop in this work was designed originally (with ONR support) as a highly-sensitive means with which to detect and identify radicals optically in environmental systems (Blough and Simpson, 1988). However, the use of this approach has expanded widely and now includes applications in the biological and health sciences (eg., Pou et al., 1993; Kalai et al., 1998; Hideg et al., 1998; Li et al., 1999a, 1999b, 2000, Lozinsky et al., 2001, Flicker and Green, 2001, Haugland, 2001) and polymer chemistry (eg., Gerlock et al., 1993; Moad et al., 1999; Ballesteros et al., 2001).

RELATED PROJECTS

In a related, ONR-supported project, we are examining the factors controlling the distribution and dynamics of CDOM in estuarine and coastal waters through a combination of field and laboratory measurements. As CDOM is the principal photoreactive constituent of most natural waters, an understanding of the factors that control its distribution in the environment is essential for determining the impact of photochemical processes in the mineralization of both natural and anthropogenic compounds.

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